Colloid & Polymer Science Colloid Polym Sci 272:25–35 (1994)

On the dielectric glass relaxation process of polymers: Ball-like labels in polystyrene

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Abstract: Ball-like molecules with strong dipoles (labels) were mixed with technical polystyrene (PS168N) in low concentrations ($< 0.5\%$ wt) and measured dielectrically in the frequency range 10^{-2}–10^{7} Hz, and the temperature range 100°–135 °C (glass relaxation region). The measurements showed that these ball-like molecules relax cooperatively with the polymeric segments with relaxation times lying at the high-frequency tail of the glass process. The activation energy of the main label process is found to be very similar to that of the glass process of the polystyrene segments and also has the same temperature dependence. This finding implies the existence of an additional mode of relaxation in the dielectric spectrum of the glass process of polystyrene (compared to polyisoprene). Considering the different behavior of the ball-like molecules in polystyrene and polyisoprene and the temperature dependence of the half-width of dielectric loss peak in different polymers, we suggest that the polymers could be classified into three classes according to the available dielectric relaxation modes in the glass process. In addition, the label molecules showed a high-frequency local relaxation process. The relaxation strength ratio of the local process (X_{local}) to the total relaxation strength of the label was found to be dependent on the volume of the label. This phenomenon could supply a new method for the determination of the mean size of the holes (voids) representing the free volume of the host matrix.

Key words: Dielectric relaxation – label – polystyrene – ball-like molecules – glass process – voids

Introduction

The reorientation of guest molecules (labels) in polymers is recognized as a method for the study of the reorientation and the packing of the polymeric segments. The label reorientations can be investigated by different methods, mainly the dielectric ([1–4], and others), and the fluorescence techniques ([5–7], and others). The labels are usually added to the polymers in very low concentrations in order to reduce their influence on the polymeric packing and also to avoid their dipole association (in the case of the labels used for the dielectric measurements).

In previous works, we reported about the dielectric relaxation of rod- and ball-like molecules in polyisoprene [4, 8]. It was found that the rod-like molecules with lengths > 10 Å relax cooperatively with the polymeric segments with relaxation times longer than that of the segments by a factor ranging between 10 and 100, depending on the length of the label (the longer the label, the greater the factor). On the other hand, the ball-like molecules were found to relax cooperatively with the isoprene segments with the same relaxation time. In addition, the ball-like molecules exhibited a local relaxation process. Hyde and Ediger [7] found that anthracene relaxes cooperatively with the segments with relaxation times very similar to those obtained dielectrically for the glass process of the segment.

The present work is a continuation of our previous investigations for the reorientation of the label molecules (different in shape, size, and length) in polymers. This study concerns the dielectric relaxation of ball-like molecules with different sizes in polystyrene. The labels used are the same as used in the previous work on polyisoprene

[8]. In this work, we aim to shed more light on the relaxation mechanism of the guest molecules in relation to the glass process of the matrix.

The choice of polystyrene as a matrix is based on the fact that 1) it is very suitable for the dielectric measurements, since it is not only nonpolar, but also the ionic conductivity in commercially available samples is low enough to detect the dipole relaxation of the segments. 2) atactic polystyrene is completely amorphous.

Experimental

Ball-like molecules with different volumes (Table 1) were dissolved in technical atactic polystyrene PS168N ($M_w = 250\,000$ g/mole, kindly provided by BASF, Ludwigshafen) in very low concentrations ($<$ 0.5% wt). The use of these low concentrations was important to obtain a height of the label relaxation process, which is still smaller than the glass relaxation process, in order to detect both relaxations. The dielectric properties of the mixtures were measured using the same equipment as described before [9] in the frequency and temperature ranges, 10^{-2}–10^{7} Hz and 100°–135 °C, respectively. The samples were prepared by dissolving the label and polystyrene in methylene chloride. Then, the solution was dropped slowly on the lower electrode surface (8-cm diameter) in the middle of a teflon ring (4-cm diameter) to prevent the spreading of the liquid. The film was left 2 days at room temperature and then dried in vacuum at 90 °C for about 6 h. Thereafter, the temperature is raised to 170 °C, the upper electrode was put (4-cm diameter) and pressed quickly to get a condenser with a capacity of 100 pF. The condenser was then transferred to the measuring cell and left with P_2O_5. It is noteworthy to state that a part of the label was inevitably evaporated, during the preparation of the measuring condenser. This is due to the high vapor pressure of the labels under the preparation conditions used. However, the use of the high vacuum and high temperature was required to get out any air bubbles or any residues of water and methylene chloride. For this reason, several trials were made to prepare samples with concentrations lower than 0.5% wt. The starting weight of the label was about 1% wt. The final weight of the additives in the condenser was calculated from the experimental total relaxation strength of the label, calculated from the peaks in Figs. 5–8 using Kramers–Kronig relation, using Fröhlich–Onsager equation for unrestricted reorientation of cyano dipoles (Table 1). The concentration of cyano dipoles was low enough, so that no orientational correlation of them can be expected [9]. The dipole moment used in the calculation was 4.128 D. The sample homogeneity was ensured by heating the sample at 130 °C for 6 h and monitoring the dielectric relaxation up to steady-state. The dielectric loss curves were analyzed by using a VAX 6440 from Digital Equipments and a powerful minimization program NAG-E04KBF from the library of the Computer Center of the University of Ulm. The program NAG-E04KBF is a comprehensive quasi-Newton algorithm for a minimization of function of several variables, and was optimized for our analysis by W. von Soden in the Department of Applied Physics, University of Ulm.

Table 1. Molecular volume of the labels

Label	Abbreviation	Concen. % wt	Volume Å
p-cyanotoluene	*p*-Tol-CN	0.1	200
1-adamantancarbonitrile	adaman-CN	0.15	238
9-cyanophenanthrene	phenan-CN	0.49	301

The volume was determined from the density values

Results and discussion

Figure 1 shows the glass relaxation process of PS168N, which is due to the micro-Brownian cooperative reorientations of the polymeric segments. It can also be seen in Fig. 1 that the shape and width of the glass relaxation process are strongly dependent on the temperature.

Figure 2 represents the mixture of 0.1% *p*-Tol-CN in PS168N. This figure shows that the relaxation maxima of the observed process are slightly shifted to higher frequencies, when compared with the pure matrix (Fig. 1) at the same temperature. It can also be observed that the height of the main peak is almost the same as that of the pure matrix. Moreover, it seems that the *p*-Tol-CN molecules relax with frequencies which lie at the high frequency tail of the glass process of the matrix. In addition, the half-width of the total process in this mixture is remarkably greater than that of the pure matrix. The measurements at temperatures

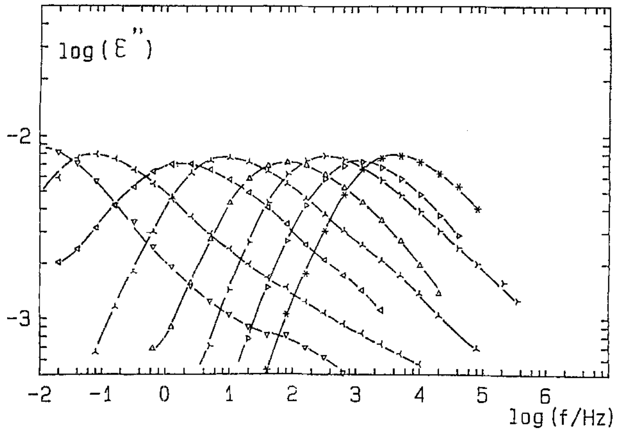

Fig. 1. Dielectric loss of technical polystyrene PS168N for the glass relaxation process with logarithmic scale over the frequency at different temperatures (∇ 101; –< 105; ◁ 110.5; ⅄ 114.5; △ 120.5; ≻- 124.5; ▷ 130; * 135 °C)

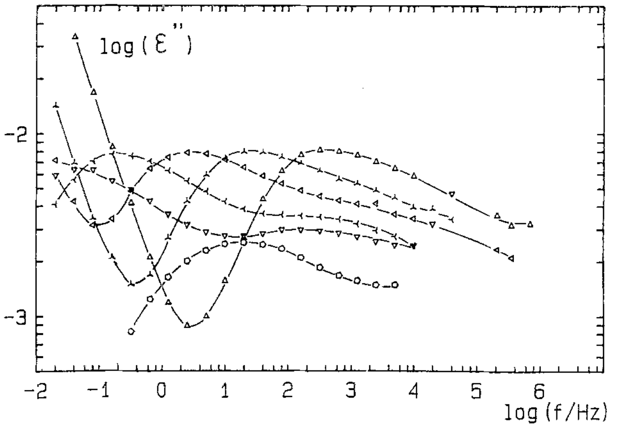

Fig. 2. Dielectric loss of 0.1% *p*-Tol-CN in PS168N (○ 72; ∇ 99.5; –< 104; ◁ 109.5; ⅄ 115; △ 122.5 °C)

below T_g show that *p*-Tol-CN exhibits a local relaxation process.

The measurements of the mixture of 0.15% adaman-CN is shown in Fig. 3. It can be seen that relaxation maxima are also shifted to higher frequencies, as in the case of the mixture with *p*-Tol-CN (Fig. 2), but the height of the total process in the adaman-CN mixture is higher than that of the pure matrix. It can also be observed that the width and shape of the total process is very similar to that of the pure matrix.

A comparison between Fig. 4, which represents the mixture of 0.49% phenan-CN in PS168N, and Fig. 1 of the pure matrix show that this label causes an increase in the width and height of the glass process. It seems also that the phenan-CN relax with frequencies which lie at the high-frequency side of relaxation of the polystyrene segments.

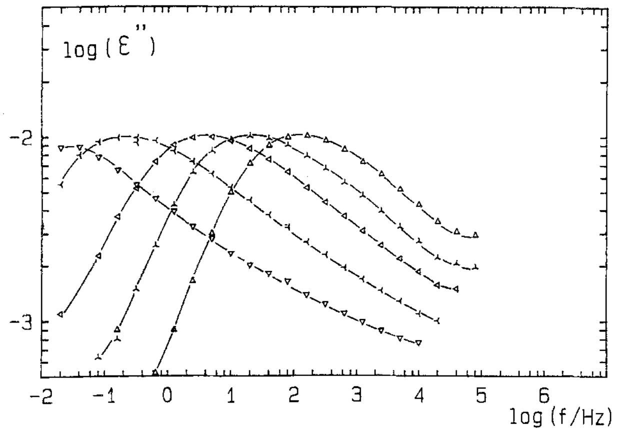

Fig. 3. Dielectric loss of 0.15% adaman-CN in PS168N (∇ 100; –< 105.5; ◁ 111; ⅄ 115; △ 120 °C)

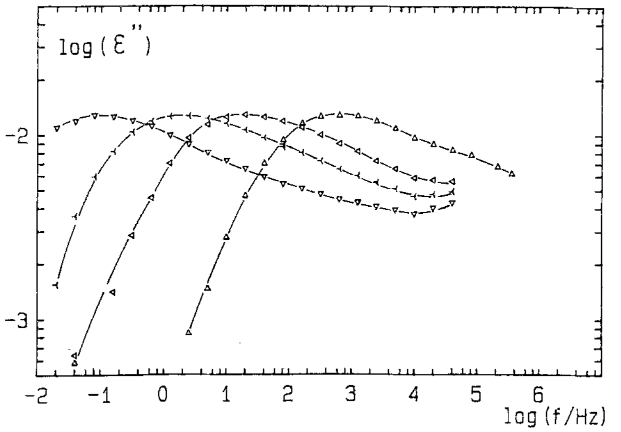

Fig. 4. Dielectric loss of 0.49% phenan-CN in PS168N (∇ 100.5; –< 105.5; ◁ 110.5; △ 120 °C)

The observed shift in the relaxation maxima to higher frequencies is due to the plasticizing effect of the low molecular weight additives on the polymeric materials, which leads also to a decrease in the glass transition temperature [10, 11]. The increase of the height of the relaxation process is an evidence of the coupling between the label reorientations and that of the polymeric segments. This finding was observed in the literature by several authors [1, 8, 12]. It was also reported earlier that small additives in polymers exhibit a local relaxation process (which is also active in the glassy state) through their partial reorientations [1, 8, 12, 13].

The effect of the additives on the width of the glass process of the polymers is still not clear in the literature [12, 14]. However, according to our experimental results for mixtures of non-polar additives and oligostyrenes with polystyrene with different concentrations (that have not yet been published), it is certain that the non-polar low molecular weight additives have no effect on the width and shape of the glass process of the matrix when they are mixed with concentrations lower than 5%.

Analysis of the measured spectrum

It is now clear that further analysis of the measured curves (Figs. 2–4) is required to separate the contribution of the segmental relaxation process of the polystyrene segments from the whole relaxation process, in order to evaluate exactly the relaxation characteristics of the label process. The basic idea of this analysis is to subtract the contribution of the styrene segments. The main problem of the analysis is that: 1) the position of the relaxation maxima of the segmental relaxation at the measured temperatures is not known exactly due to the plasticizing effect of the labels on the matrix; 2) the width of the glass relaxation process of the matrix is strongly dependent on the temperature.

It has been found that the shape and width of the glass relaxation process of different plasticized polystyrenes are the same if the peak appears in the same frequency range, regardless of the difference in the glass transition temperature and the molecular weight of the polymer as well as the temperature of measurements [15]. This means that if the relaxation frequency of the glass process of the matrix at a given temperature is known, one can use the shape parameters of the glass process of the pure matrix at the corresponding relaxation frequency as known parameters for the analysis routine [15]. This means that the determination of the maximum frequency of the plasticized polystyrene in the mixtures is now the main difficulty in the analysis.

One of the possible methods is based on the calorimeteric glass transition temperature of that polymer. This method is described in another work [15]. In the present case, however, we were not able to determine the calorimetric glass transition temperature of the mixtures, because the label evaporated to some extent during the DSC measurements. It must be stated here that the dielectric measurements of the samples are reproducible when repetition was made. This means that the label molecules did not evaporate during the dielectric measurements.

In order to overcome the difficulty of the determination of the relaxation maxima, the label concentrations used here were very low ($< 0.5\%$ wt), so that the peak maxima of the total process are mainly due to the segmental relaxation of the matrix. The estimated positions of the glass process of the matrix at the concentrations used have an accuracy better than ± 0.2 decades. This is enough for determining the shape parameters for the contribution of the matrix at the temperature of measurement.

The glass process of the pure polystyrene was fitted using two symmetrical relaxation processes according to the formula of Cole-Cole at different temperatures as applied and discussed in our previous work [8]. Thus, the shape and relaxation strength of the contribution of the matrix were represented by given parameters. The position along the frequency axis, however, was a free parameter in the final fit procedure for the mixture.

The contribution of the labels was simulated also by two symmetrical processes, one represents the low frequency cooperative process (main), while the other represents the high-frequency one (local) [8]. The symmetrical representation (instead of an asymmetric one) of the main process of the label was required to reduce the uncertainty factor of the analysis by decreasing the number of unknown parameters.

Some representatives of the analysis plots of the mixtures are shown in Figs. 5–8. The graphic symbols are the experimental points. The line drawn through the experimental points is the summation of the glass process of the matrix and the label relaxation. It can be seen that this line fits the experimental points with a fair accuracy for all the analyzed curves (see Figs. 5–8).

The activation energy curves of the different processes obtained from the analysis for the different labels in comparison with that of the pure matrix are presented in Fig. 9. The filled symbols

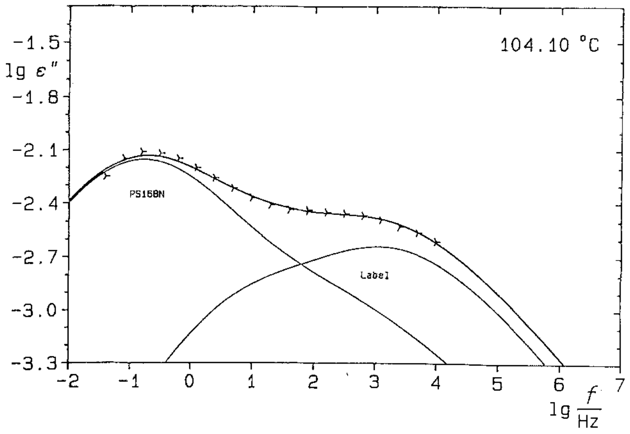

Fig. 5. Analysis plot of 0.1% *p*-Tol-CN in PS168N at temperature 104.1 °C. The contribution of each component (label as well as PS168N) is represented as the sum of two coupled relaxation processes after Cole and Cole

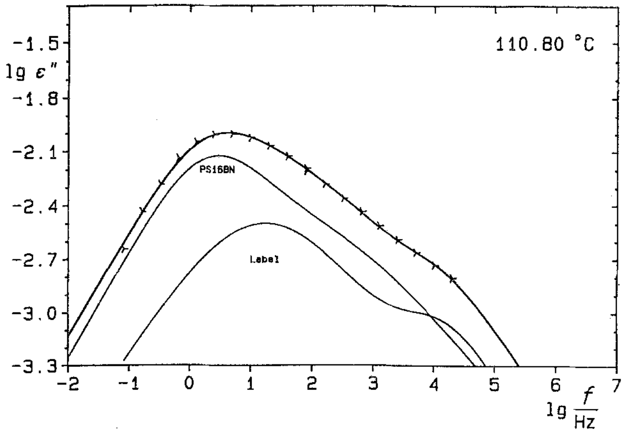

Fig. 7. Analysis plot of 0.15% adaman-CN in PS168N at temperature 110.8 °C

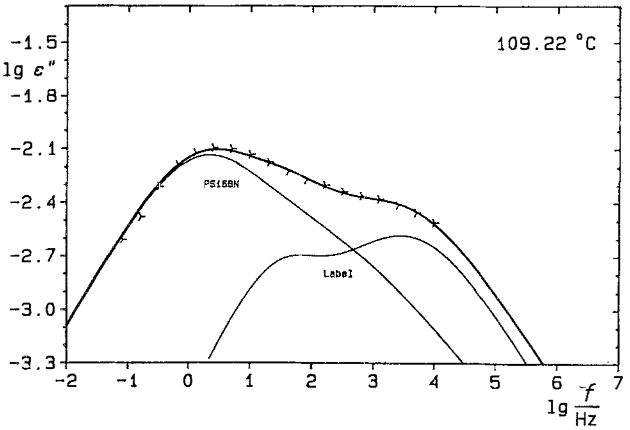

Fig. 6. The same as Fig. 5, but at temperature 109 °C

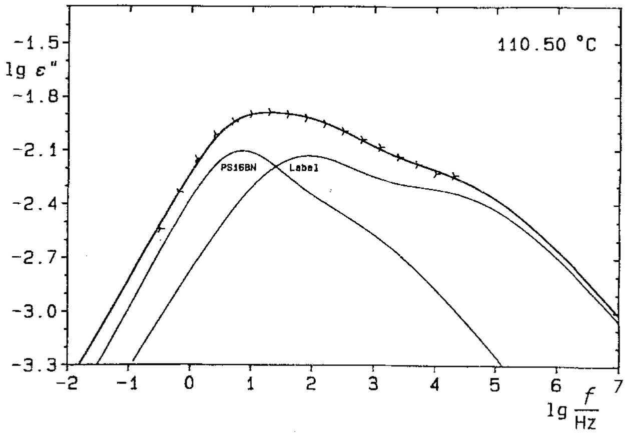

Fig. 8. Analysis plot of 0.49% phenan-CN in PS168N at temperature 110.5 °C

represent the glass process of the polystyrene in the mixtures, while the unfilled symbols represent the label processes. This figure shows that the segmental relaxation process of the matrix is shifted to higher frequencies due to the addition of the labels. This shift depends on the label concentration, as obtained from the measurements at different concentrations. This is due to the plasticizing effect of labels on the matrix [10, 11]. It can also be observed that the activation curves of the low-frequency process of the labels has nearly the same slope as the glass process of the matrix. This implies that this low-frequency process of the label is a cooperative relaxation process and must be coupled tightly with the cooperative reorientations of the segments.

On the other hand, the temperature dependence and the position of the high-frequency process are comparable to that of the local relaxation of polymers [16]. In addition, the half-width of this process is rather large (the Cole–Cole parameter $(1-\alpha)$ is in the range of 0.4). Therefore, this relaxation process is attributed to the local reorientations of the dipoles. The local relaxation process of additives was detected by several authors in polymers [1, 8, 12, 13], as well as in low molecular weight organic glasses [17, 18].

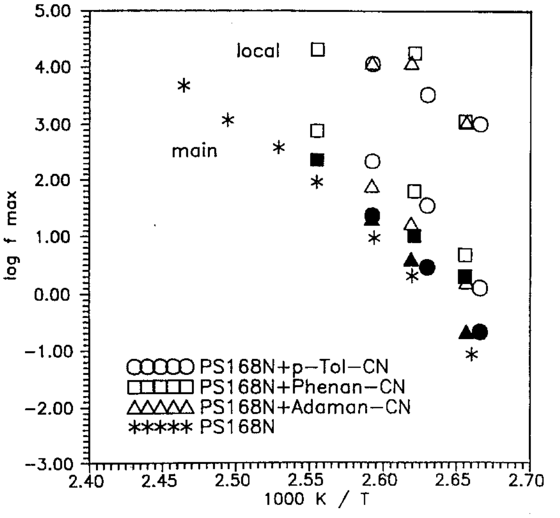

Fig. 9. The activation energy diagram of different samples; the filled symbols represent the matrix contribution, while the unfilled represent the label processes

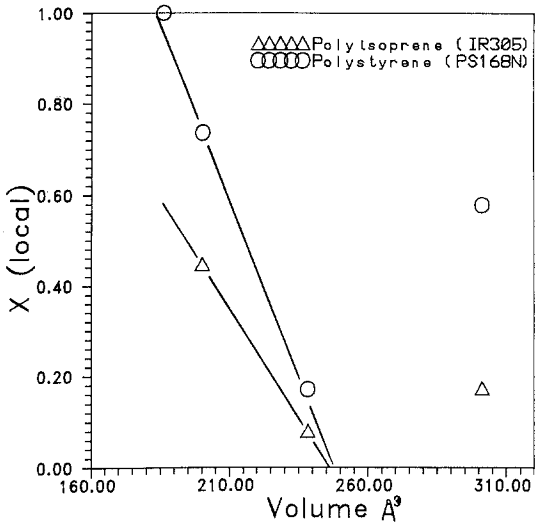

Fig. 10. A plot of X_{local} versus the volume of the labels in Å^3

The local relaxation of the label

It has been found that, in the case of polyisoprene, the local contribution of the label X_{local}, which can be represented by the ratio of the relaxation strength of the local process to the total one of the label, decreases with increasing the label volume for the labels with the same shape [8]. For comparison, a plot of the parameter X_{local} versus the label volume is presented in Fig. 10 for different labels in polyisoprene and polystyrene. A literature point of *o*-dichlorobenzene in polystyrene is also included [19]. The X_{local} values of phenan-CN deviate from the other labels for both matrices. This could probably be attributed to the difference in the shape between phenan-CN and the other labels, since phenan-CN is more disc-like than spherical. As a consequence, the decrease in the local contribution of the spherical label molecules with increase of their volume could supply a new method for the determination of the mean size of the holes (voids) in polymers. On the other hand, the volume dependence of X_{local} (slope of the lines in Fig. 10) could probably supply a measure for the distribution of hole sizes in the different polymers. The average value of the hole sizes is found to be dependent on the matrix: 185 Å^3 in polyisoprene and 205 Å^3 in polystyrene. It is clear that this investigation must be extended for other labels with different sizes and also for other polymers.

The cooperative process of the label

Hains and Williams have measured the reorientations of small polar additives with different concentrations (9.6–100% wt) in polystyrene [12]. They found that: 1) the low concentrations of the polar additives ($<$ 14% wt) showed no phase separation; 2) the ε''_m of the main relaxation process inceased with increasing the concentration of the additives; 3) the additives showed also a local relaxation process; 4) the total relaxation process of the label (for concentrations $<$ 14%) was very broad and the half-width was more than five decades; 5) the activation energy of the glass process of the mixtures (this process is mainly due to the label reorientations since the lowest label concentration was 9.6% wt) is almost constant (the expected decrease in the activation energy, due to the plasticizing effect of the additive, was not observed because they have determined the activation energy at relatively high frequencies (0.1–10 kHz)). These findings of Hains and Williams are in complete agreement with our present measurements.

It can be seen again in Fig. 9 that the main label process has the same slope (i.e., the same activation energy) as the plasticized polystyrene. But, the use of extremely low concentrations of the label has revealed that the label relaxes with frequencies higher than those of the glass relaxation process. This is in contrast to our dielectric measurements of the same labels in polyisoprene [8]. We found that they relax cooperatively with the segmental relaxation of the polyisoprene and at the same relaxation frequency [8]. Furthermore, Hyde and Ediger have used their sophisticated optical technique to find out that the chromophors used (8–12 Å) relax cooperatively, with the isoprene segments with relaxation times in a good agreement to that measured dielectrically [7]. They concluded that the kinetic segment involved in the dielectric glass process must be in the order of the size of the anthracene or approximately two monomers. Also, Adachi and coworkers reported that slightly more than one monomer unit is involved in the dielectric glass process based on a comparison between the segmental relaxation time and the normal mode relaxation in the bulk of polyisoprene [20].

But, in case of polystyrene the ball-like molecules relax through a cooperative relaxation process with relaxation frequencies lying at the high-frequency tail of the glass process of the matrix. This finding is very surprising, since it stands in contrast to the results obtained not only in polyisoprene, but also in case of low molecular weight organic glasses [17]. In addition, the activation energies of the cooperative relaxation process of the labels are very similar to those of the glass process of the matrix; the curves are only shifted on the frequency axis. It is very important to find out whether the value of $\Delta \log f_m$ ($\log f_m$(label) − $\log f_m$(glass process of matrix)) is dependent on the size of label or not. For a better comparison of different labels with different plasticizing effect, the maximum frequency of the cooperative relaxation of the label is plotted over the maximum frequency of the matrix (Fig. 11) for all of the three labels measured here at different temperatures. This new type of plot is based on the experimental fact that the glass processes of polystyrenes with different molecular weights (and also with plasticizer content < 10% wt) which appear at the same relaxation frequency have the same half-width and the same shape. This means that they the have the same distribution of relaxation times [15]. This new type of plots has the advantage that the plasticizing effect can be eliminated so that different molecular weights or plasticized polymers can be easily compared at different temperatures. It can be seen in this figure that the relaxation frequencies of all ball-like molecules can be represented by a straight line which has a very similar slope to that of the matrix (the diagonal line in the figure). These experimental facts imply the following:

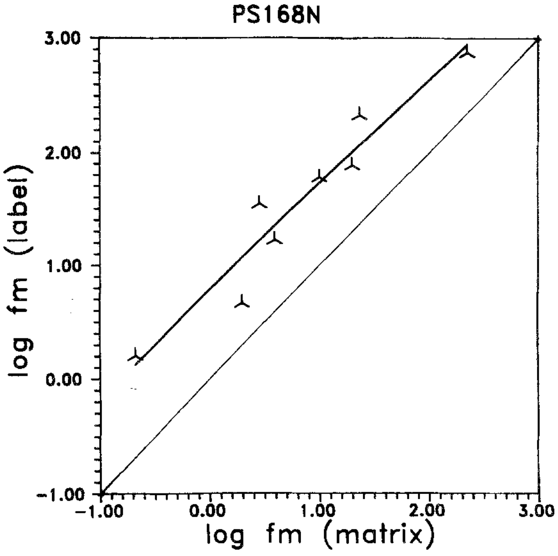

Fig. 11. The logarithm of the maximum frequency for the cooperative part of the label peak plotted over the maximum frequency for the total contribution of the matrix

1) the size of the label molecules plays no role for the determination of the relaxation frequency maximum of the cooperative relaxation process of labels in relation to that of the glass process of the matrix.
2) All the labels used detect the same relaxation mode, which represents an elemental relaxation mode in the spectrum of the glass process.
3) the main part of the dielectric glass relaxation of polystyrene has relaxation times longer than those of the elemental mode.
4) the ratio of the relaxation times of the two modes is almost temperature independent.

In order to understand this phenomenon, we used the semi-empirical potential energy calculation of isotactic and syndiotactic polystyrene made by Beck [21]. These calculations showed a helix-like structure in which the phenyl rings of the styrene segments make an angle with the vertical axis of the polymer chain, so that the final appearance of the polystyrene chain can be regarded as a "Christmas tree". This implies that the phenyl groups must have two dipole components (vertical and longitudinal to the chain axis). Therefore, the glass process must include both relaxations of these two components, because polystyrene exhibits no separate relaxation process of the longitudinal component like polyisoprene. In the case of polyisoprene, the relaxation of the longitudinal dipole moment can only be achieved through a diffusion mechanism [20, 22, 23] with relaxation times longer than those of the glass process by several decades. The molecular weight dependence of $\Delta \log f_m$ for polyisoprene can be attributed to the fact that the direction of the longitudinal component of the dipoles is fixed by the asymmetry of the monomeric units in combination with the dipole bonds along the chain. The almost head-to-tail configuration of the monomeric units means that the relaxation of the longitudinal component can only be achieved by a slow diffusion mechanism (reptation) [22, 23] involving the whole chain.

In the case of polystyrene, the relaxation of the longitudinal components (the change of the directions of the branches of the "Christmas tree") can occur, for example, by simultaneous motion of a limited number of segments (as shift of helix defects). This conformational change from right- to left-handed helix and vice versa can even occur in crystalline isotactic polystyrene when annealed in the neighborhood of the melting temperature [24].

Accordingly, one would expect that the polymers could be classified into three classes depending on the available segmental modes in the glass process. The first class includes the polymers with a longitudinal dipole component that can relax only by a diffusion (reptation) motion of the whole chain (change of the end-to-end vector) such as polyisoprene. The second class of polymers includes the polymers which have a longitudinal dipole component along the chains that can relax by a change of helix type, which means with conformational changes of the chain by the cooperative reorientation of a limited number of segments (polystyrene PS, polyvinyl chloride PVC). In addition, there are polymers in which the dipole is located in the side chain (like PVAc and PMMA). The longitudinal component of these dipoles is expected to relax as fast as the vertical component. Therefore, the dielectric spectrum of the glass process in this third class of polymers is probably not influenced by the longitudinal dipole component and a spectrum similar to that of the vertical component (segmental mode) of the first class of polymers is expected.

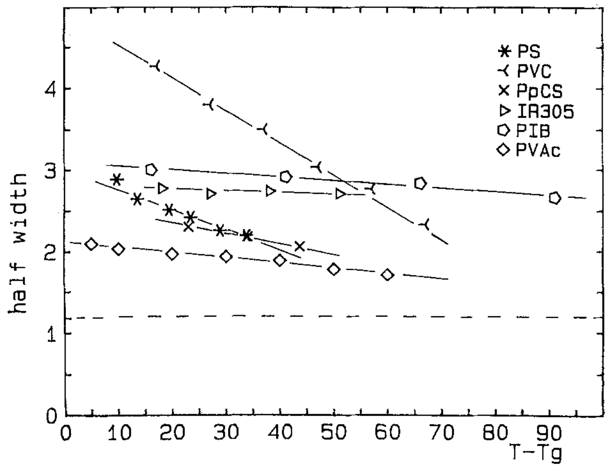

Fig. 12. Half-width, measured in decades, of the main dielectric loss peak, plotted over the difference between the temperature of measurement and the glass temperature, for * polystyrene, ≻– polyvinyl chloride, × poly parachlorostyrene, ▷ synthetic cis-polyisoprene, ○ polyisobutylene, ◇ polyvinyl acetate

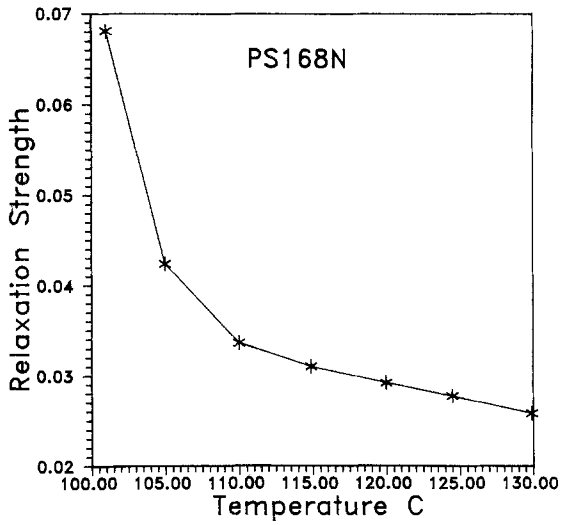

Fig. 13. Total relaxation strength of the glass relaxation (main relaxation) process in PS168N

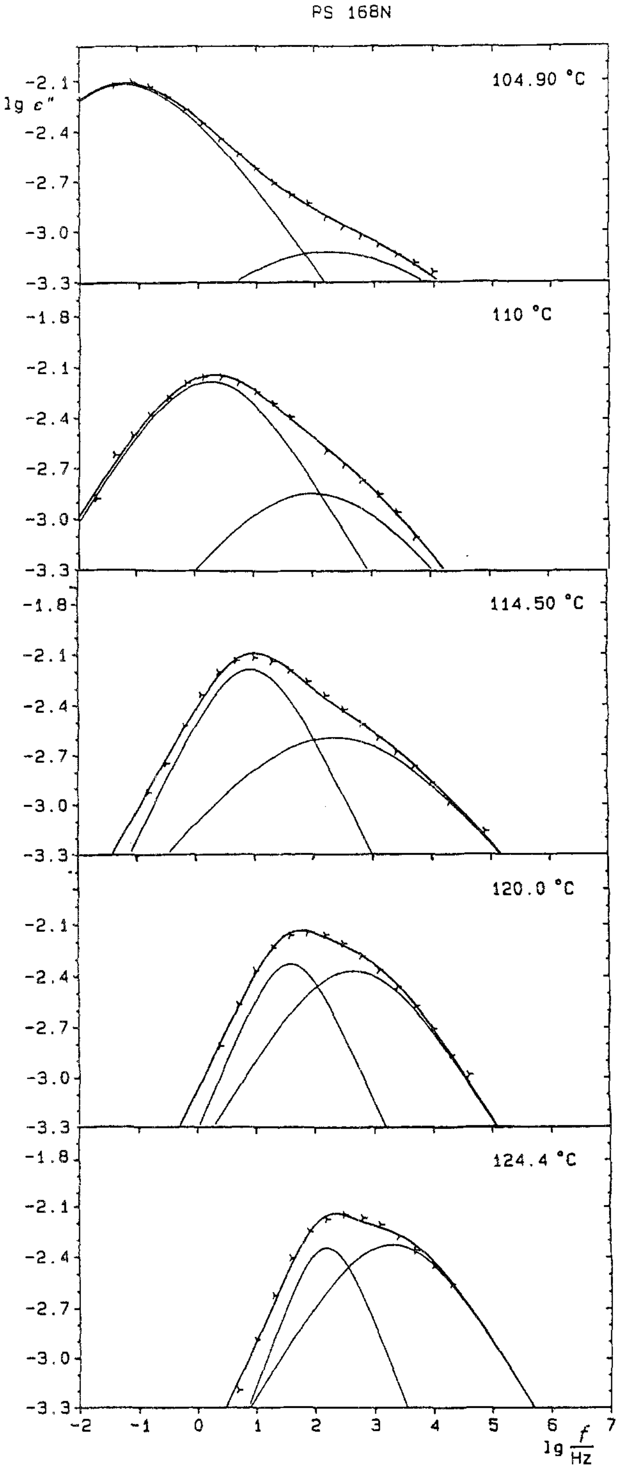

Fig. 14. Analysis plot of the glass relaxation process of the pure polystyrene PS168N in two relaxation processes at different temperatures.

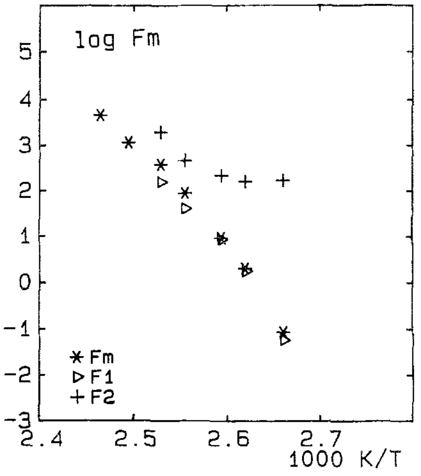

Fig. 15. The activation energy diagram of the different modes of relaxation in polystyrenes (▷, +) and the total maximum (∗)

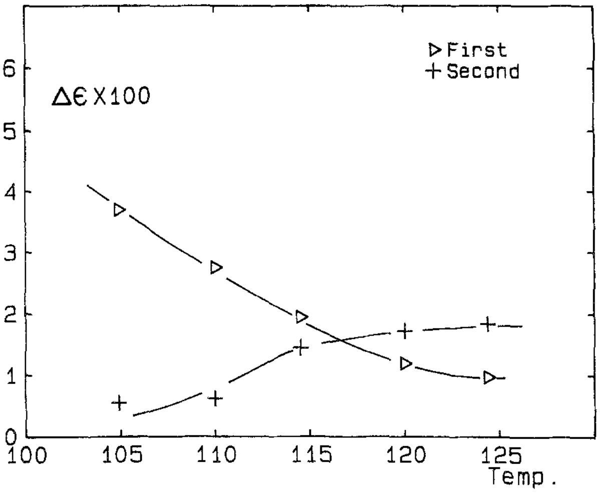

Fig. 16. The temperature dependence of the relaxation strength for the different relaxation modes

This classification implies that the temperature coefficient of the half-width of the polymers of the second class must be greater than that of the first class. This is because the coupling of the longitudinal components of the neighboring segments decreases at high temperatures. In fact, this is in agreement with the experimental results (see Fig. 12). In addition, the interpretation that the relaxation of the longitudinal component is included in the spectrum of the glass process is also supported by the experimental fact that the relaxation

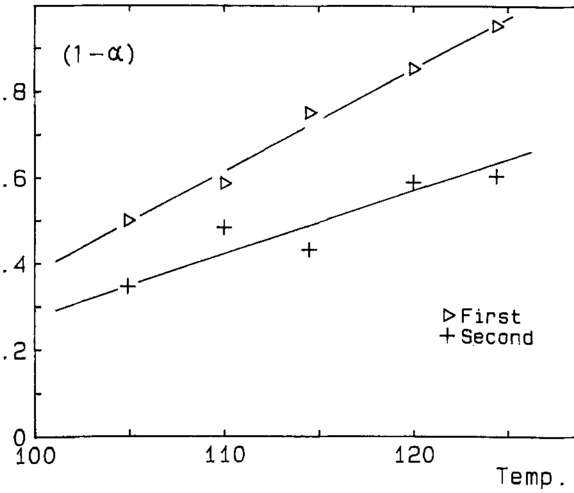

Fig. 17. The temperature dependence of the Cole-Cole shape parameters (1 − α) for the different relaxation modes

strength of the glass process of polystyrene is not linearly dependent on the reciprocal of the temperature as predicted by Fröhlich–Onsager theory (see Fig. 13). This behavior can be attributed to the fact the increase of temperature increases the concentration of the helix defects and this means a decrease in the value of $g\mu^2$ (effective dipole moment in Fröhlich–Onsager equation) by the decrease in the degree of association of the relaxing units. Unfortunately, an exact analysis for the spectrum of the glass process into different relaxation modes can not be achieved. This is because the spectrum of the glass process probably consists of three relaxation modes of the segments; the Christmas tree mode (longitudinal component) and two modes for the vertical component [27], where each of them has its own relaxation parameters (three parameters). For this reason, as a simplification and also to reduce the uncertainty factor of the analysis, the glass process of pure polystyrene is analyzed into two symmetrical process (Fig. 14). At relatively high temperatures ($> 110\,^{\circ}C$) the low-frequency process is mainly influenced by the "Christmas tree" relaxation, while the high-frequency process mainly originates from the relaxation of the vertical dipole component of the segments. On the other hand, at temperatures $\leq 105\,^{\circ}C$ the high-frequency process is mainly affected by the high-frequency mode of the vertical dipole component of the segments, i.e., the third relaxation mode which originates from the fluctuation of the dislocation network near the glass temperature [27]. The analysis results are represented in Figs. 15–17. Accordingly, one would expect that at extremely high temperature or in dilute solutions, the contributions of Christmas-tree-relaxation must completely vanish. This expectation is in agreement with the experimental results obtained by Mashimo and Chiba [28]. The dashed line in Fig. 12 represents the half-width of four polymers measured by Mashimo and Chiba [28] in dilute solutions. They found [28] that the shape and asymmetry of the glass relaxation of the following polymers PVAc (third class), PVC, PpCS (polyparachlorostyrene), and PpBS (polyparabromostyrene) (second class) are the same irrespective of the polymer, solvents, and temperature. In addition, they have found no molecular weight dependence. Thus, the half-width in dilute solution seems to represent the limit for (hypothetical) extremely high temperatures.

Acknowledgement

The Deutscher Akademischer Austauschdienst is gratefully acknowledged for the grant given to A. A. Mansour.

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Received March 25, 1992;
accepted March 12, 1993

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